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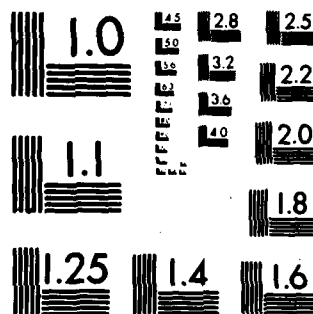
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FINAL REPORT - NOVEMBER 21, 1980

Title: "Semiconductor/Liquid Junctions: Molecular Manipulation of  
Interface Energetics"

Contract No.: N00014-78-C-0630

Project No.: NR 051-696

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Accomplishments (8-01-78 - 7-31-80, Contract No. N00014-78-C-0630)

THE Research carried out during the two year period 8-01-78 - 7-31-80 focused on n-type semiconducting photoanodes prepared from naturally occurring, single-crystal  $\text{MoS}_2$  and synthetic single-crystal  $\text{MoSe}_2$ . Work on "textured" single-crystal (100) Si was initiated under contract N00014-78-C-0630 and continued under contract N00014-75-C-0880, project no. NR 051-579. <sup>AND</sup> Additionally, preliminary study of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photoanode surfaces revealed interesting behavior that is being pursued under contract no. N00014-75-C-0880, project no. NR 051-579. The highlights of our accomplishments in these areas are given in the paragraphs below.

N-Type  $\text{MoY}_2$ /Liquid Electrolyte Junctions. N-type  $\text{MoS}_2$  and  $\text{MoSe}_2$  have been characterized in  $\text{CH}_3\text{CN}/0.10 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$  electrolyte solutions containing various redox reagents.<sup>1-3</sup> The use of  $\text{CH}_3\text{CN}$  allows the examination of a wider range of redox reagents than is possible in  $\text{H}_2\text{O}$ ; we found that both n-type  $\text{MoS}_2$  and  $\text{MoSe}_2$  resist photoanodic decomposition in  $\text{CH}_3\text{CN}$  compared to  $\text{H}_2\text{O}$ . It would appear that the rationale rests in the fact that the energetics for photoanodic decomposition depend strongly on the solvation energy for the various products.<sup>4</sup> The fact is that  $\text{MoS}_2$  and  $\text{MoSe}_2$  exhibit photoanodic decomposition in  $\text{CH}_3\text{CN}/0.10 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$  at a  $\sim 0.5 \text{ V}$  more positive potential than in aqueous electrolyte. We discovered that  $\text{MoS}_2$  and  $\text{MoSe}_2$  photoanodes could be used to effect the uphill  $2 \text{ Cl}^- \rightarrow \text{Cl}_2$  process, without destruction of the photoanode at a  $\text{Cl}^-$  concentration where no  $\text{Cl}_2$  is generated (only photoanodic decomposition of the electrode is observed) in aqueous solution.

Characterization of the interface energetics for  $\text{MoS}_2$  and  $\text{MoSe}_2$  was in fact the foundation for a study aimed at showing that surface modification could inhibit the effect of  $\text{I}^-$  adsorption in aqueous solution. The adsorption of  $\text{I}^-$  in aqueous solutions gives an  $\sim 0.5 \text{ V}$  shift in the flat-band potential

for  $\text{MoS}_2$  or  $\text{MoSe}_2$ .<sup>5</sup> Preliminary experiments showed that ferrocene-based redox reagents<sup>6</sup> could be used to functionalize the surface of both photoanodes. Polymeric quantities of a ferrocene reagent could be anchored to the surface; the reduction of N,N'-dimethyl-4,4'-bipyridinium could be inhibited; but the behavior of  $\text{I}^-$  was not significantly affected. Such data suggest that the  $\text{I}^-$ , but not the N,N'-dimethyl-4,4'-bipyridinium reagent, could penetrate through the surface-confined polymer. These studies are continuing under contract no. N00014-75-C-0880, project no. NR 051-579.

Textured <100> Si/Liquid Electrolyte Junctions. Previous work established<sup>7</sup> that <100> single-crystal Si can be chemically etched to reveal <111> planes resulting in a "textured" surface that has lower specular reflection and higher effective surface area than polished <100> Si. We initiated a study, completed under contract no. N00014-75-C-0630, project no. NR 571-696, to demonstrate that "textured" n-type Si can be exploited to improve performance of photoelectrochemical devices.<sup>8</sup> Work on p-type Si shows that it too can be improved by the texturing procedure.

N-Type  $\text{TiO}_2$  and  $\text{SrTiO}_3$  Surfaces. One of our initial objectives was to exhaustively functionalize an n-type semiconducting oxide surface to remove all sites of protonation/deprotonation equilibria. Both n-type  $\text{TiO}_2$  and  $\text{SrTiO}_3$  have been successfully functionalized using a hydrolytically unstable ferrocene reagent that should react with the surface-OH groups. Part of the strategy in using the ferrocene-based reagent was that  $E^\circ(\text{ferricenium/ferrocene})$  is very close to the position of a postulated surface state of  $\text{TiO}_2$ .<sup>9</sup> During the preliminary studies of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  in  $\text{CH}_3\text{CN}/0.10 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$  we discovered two important facts: (i) the heterogeneous oxidation of ferrocene at illuminated n-type  $\text{TiO}_2$  or  $\text{SrTiO}_3$  is exceedingly slow compared to the rate at n-type Si, GaAs, InP; (ii)  $\text{TiO}_2$  and  $\text{SrTiO}_3$  appear to be "Fermi level pinned"<sup>10</sup> when contacting liquid electrolyte solutions having  $E_{\text{redox}}$  more positive



than  $\sim 0.0$  V vs. SCE. Both of these discoveries afford us a special opportunity to add to the understanding of interface energetics for these metal oxide semiconductors. The Fermi level pinning and slow photooxidation suggest a rather specific surface state distribution. This issue is being elaborated under contract no. N00014-75-C-0880, project no. NR 051-579.

### References

1. Schneemeyer, L.F.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 6496.
2. Schneemeyer, L.F.; Wrighton, M.S.; Stacy, A.; Sienko, M.J. Appl. Phys. Lett., 1980, 36, 701.
3. Schneemeyer, L.F.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 0000.
4. (a) Bard, A.J.; Wrighton, M.S. J. Electrochem. Soc., 1977, 124, 1706;  
(b) Gerischer, H. J. Electroanal. Chem., 1977, 82, 133;  
(c) Park, S.-M.; Barber, M.E. J. Electroanal. Chem., 1977, 99, 67.
5. Gobrecht, J.; Tributsch, H.; Gerischer, H. J. Electrochem. Soc., 1978, 125, 2085.
6. Wrighton, M. S.; Palazzotto, M.C.; Bocarsly, A.B.; Bolts, J.M.; Fischer, A.B.; Nadj, L. J. Am. Chem. Soc., 1978, 100, 7264.
7. (a) Kern, W. R.C.A. Review, 1978, 39, 287; (b) Baraona, C.; Brandhorst, H. 11th IEEE Photovoltaic Specialists Conference, 1975, 44.
8. Bruce, J.A.; Wrighton, M.S. J. Electroanal. Chem., 1981, 00, 0000 [in press].
9. Frank, S.N.; Bard, A.J. J. Am. Chem. Soc., 1975, 97, 7427.
10. Bard, A.J.; Bocarsly, A.B.; Fan, F.-R. F.; Walton, E.G.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3671.

Research Personnel (Contract No. N00014-78-C-0630)

Mark S. Wrighton, Professor of Chemistry, Principal Investigator

Lynn F. Schneemeyer, Ph.D., Postdoctoral Research Associate

James A. Bruce, Graduate Research Assistant

Technical Reports (Contract No. N00014-78-C-0630) (with Journal Reference)

- ONR-TR-1 "Flat-Band Potential of n-Type Semiconducting Molybdenum Disulfide by Cyclic Voltammetry of Two-Electron Reductants: Interface Energetics and the Sustained Photooxidation of Chloride", Lynn F. Schneemeyer and Mark S. Wrighton. (Published: J. Am. Chem. Soc., 1979, 101, 6496.)
- ONR-TR-2 "Photoelectrochemical Conversion of Optical Energy to Electricity and Fuels", Mark S. Wrighton. (Published: Acc. Chem. Res., 1979, 12, 303.)
- ONR-TR-3 "N-Type Molybdenum Diselenide-Based Liquid Junction Solar Cells: A Non-Aqueous Electrolyte System Employing the Chlorine/Chloride Couple", Lynn F. Schneemeyer, Mark S. Wrighton, Angelica Stacy, and Michell J. Sienko. (Published: Appl. Phys. Lett., 1980, 36, 701.)
- ONR-TR-4 "n-Type Molybdenum Diselenide-Based Photoelectrochemical Cells: Evidence for Fermi Level Pinning and Comparison of the Efficiency for Conversion of Light to Electricity with Various Solvent/Halogen/Halide Combinations", Lynn F. Schneemeyer and Mark S. Wrighton. (Published: J. Am. Chem. Soc., 1980, 102, 0000.)

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